The Influence of Anthropogenic Activity on Heavy Metal Content of Soils in Industrial and non-Industrial Areas

by

Leonard Ulai anak Salamat

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the requirements for the
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CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

_____
(Dr. Nurlidia bt. Mansor)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

LEONARD ULAI ANAK SALAMAT

ABSTRACT

Limited record or data about the contents of heavy metal in the atmosphere within the industrial sector in Malaysia has given a platform to perform a research about the impact of anthropogenic activity. Heavy metals are increasingly released into environment due to the rise in anthropogenic activities such as industrialization. Heavy metals are released into the atmosphere and finally deposited by wet and dry deposition into soils. This research focuses on the heavy metal contents in the atmosphere at industrial and non-industrial areas. In this research, samples of soils, acts as a medium to investigate the contents of heavy metals in atmosphere. The soils samples are taken from industrial and non-industrial areas and analyzed using Flame Atomic Absorption Spectrometry (FAAS). The result from the samples will give the total concentration of heavy metal content in the atmosphere and compared between all samples taken from the industrial and non-industrial areas. This research may reflect the anthropogenic activity of industrialization and its impact towards the environment. This research will also provide the data of heavy metal concentration levels and can be future references that indicate the level of heavy metal in the environment at industrial and non-industrial areas.

ACKNOWLEDGEMENT

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INTRODUCTION

1.1 INTRODUCTION

Environmental issue is now one of the main concerns in Malaysia. Most academician, industrialist and environmentalist are becoming more aware and focused on various issues that concern the environment. This study is still new and Malaysia is still developing in the industrialization sector. In Malaysia, there are currently no soil quality reference values for heavy metals (Bernhard A. Zarcinas *et al.*, 2003). Hence, lack of information in Malaysia about heavy metal contamination on soil cause limit of sources of material for references that relevant to this studies.

Malaysia has experienced phenomenal economic growth in the last two decades. It has undergone a major structural transformation, moving from agriculture to manufacturing-based economy with significant social changes. This rapid development has brought about significant impacts to the natural environment (Shafari Che Hashim, 2000). These mean that Malaysia already in industrial revolution from past two decades and the increment of emission into the atmosphere is because of the rapid growth of industrial activity. To an industrial complex, the raw materials and end of products of which can contaminate the surrounding areas via atmospheric pollution and effluents (F. A. Vega *et al.*, 2007). An increase in contaminant emission may pose substantial implication on the environment, as heavy metals may enter and accumulate through irrigation and atmospheric deposition, which could enhance the risk of metal contamination (S. C. Wong *et al.*, 2001). Thus, effects of concentration of heavy metal in atmospheric, deposited, and then, will give the impact to the environment that may cause the air pollution increase together with the soil pollution.

The basic idea of this study is to make a comparison of sample soil that is taken from various industrial and non-industrial areas. Industrial area refers to the area that high human activity for example, factories area. Meanwhile, non-industrial refers to the area that low human activity. This study will involve field activity which is collecting soil samples and experimental to analyze the sample. The parameter that used as a finding of this study is the amount of heavy metal content in soils such as Lead (Pb), Nickel (Ni), Zinc (Zn) and Cadmium (Cd).

World soils have been seriously polluted by Pb and Cd and slightly by Zn. Pb are known to be the earliest metals utilized by humans. Cd is mainly as a by-product of zinc ore. Emission from coal-fired electric power plant represents one of largest sources categories of Mercury (Hg) emission associated with emission of Ni to the atmosphere (Han *et al.*, 2002)

The sample will be analyzed using Flame Atomic Absorption Spectroscopy (FAAS). Then, the result that achieve from this study can be determined to be a future references to create and impose any monitoring and control measurement on the environmental pollution in Malaysia.

1.2 PROBLEM STATEMENT

The increase of industrial sector in Malaysia will increase the content of heavy metal in the atmosphere. Thus, the level of heavy metal that deposited in soils may also increase. Heavy metals are emitted into the atmosphere through human activities, such as combustion of coal, mining, and processing, are transported globally and are finally deposited by wet and dry processes into the soil (Nriagu, 1979; Nriagu and Pacyna 1988; Bewers *et al.*, 1987; Han *et al.*, 2002). The emission generally is in the form of very tiny particle which may contain of heavy metal component; which combined with the dust or solid particle in industrial emission activities, are released into air. As time goes on accompanied with the effect of gravitational force and dropping of rain water, the particle will deposited onto soil from the air and diffusion, adsorption, infiltration and other mechanism occur through the soil (Mirsal, 2008). As a result, the soil pollution is greatly to occur as the effect of industrial emission. Increased input of heavy metals in environment due to rapid industrialization coupled with inadequate environmental management in the developing country like India, has led to large-scale pollution of the environment. (Srinivasa Gowd S. *et al.*, 2009). In other word, the increment of industrial activity is proportioned with the increment of industrial emission thus increases the heavy metal content in atmosphere.

1.3 OBJECTIVE

The objectives of these studies are:

1. To investigate the impact of industrial activity towards the environment.

2. To identify the presence of heavy metals in soils at industrial and non-industrial areas.

3. To compare the concentration of Lead (Pb), Nickel (Ni), Zinc (Zn) and Cadmium (Cd) content in soils at industrial and non-industrial areas.

1.4 SCOPE OF STUDY

This study will involve the field and laboratory work. For field work, soil sampling activities will be conducted at industrial area and non-industrial area. Six samples of soils taken from three sample point at industrial area. Four samples of soils taken from two sample point at non-industrial areas. For laboratory work, the study involves the solid matter investigation using particular procedures and equipment such as Flame Atomic Absorption Spectroscopy (FAAS) and pH meter. The study will focus on determining and analyzing the heavy metal content of soils in the sample and relate the finding with the influence of anthropogenic activity.

CHAPTER 2

LITERATURE REVIEW

Malaysia experienced an industrial revolution last two decades, since 1985 until now; from agriculture industry to manufacturing-based industry (Shafari Che Hashim, 2000). With the growing of number of industry around Malaysia from year to year; there is an impact to the environmental due to emission from industrial activity. The Southeast Asian region is currently undergoing rapid development and extensive changes to the social and economic structure. An increment in the size of urban population and urban centers will result in an increase in industrial and municipal waste (Zarcinas *et al.*, 2003).

Virtually all countries begin their economic development with primary type industries and slowly progress up the levels. Some tertiary industries may develop early on to support primary and secondary industries. Some will never pass secondary while others will quickly move to quaternary type industries. With industrialization, great amounts of heavy metals have been excavated and released on the surface of the earth and dispersed into the soil (Han *et al.*, 2002).

The scale of industrial production world wide seems set for inexorable growth. Developing countries clearly aim to achieve the levels of material prosperity enjoyed in the developed countries and they intend to do it by industrialization. Leaving aside environment concerns, simple equity argues that it is also morally unavoidable (Shen, 1999). Even though size of industry is the different in industry activity such as secondary industry, for example steel manufacturing industry is bigger than primary industry which is mining industry; it is the same issue occurs where is the releasing of gas emission that may impact the environment. The damage of soil in those ancient days was of a limited scale, yet since the beginnings of the industrial revolution it has taken dimensions that are hardly controllable in modern times. The main sources of urban soil pollution, however, are power generation emissions, release from transport

means and waste disposal. Electric power generation in coal-fired power plants contributes not only to the addition of inorganic and organic pollutants to the soil through air born fly ash, but also adds to the radioactive nuclide content of the soil. The industrial activity such power generation not only release the gas emission of heavy metal, but some particle that combine with the other particle in gas emission may be a radioactive particle that affect the air quality. The heavy metals in air may be introduced into the soil either directly or as fallout (dry deposition), because of the effect of gravitational forces, or in a wet form after being dissolved in precipitation, such as rain droplets (Mirsal, 2008). **TABLE 1** shows the ratio of heavy metals in emission from coal-fired power stations in comparison to the content of the same in total emission in West Germany.

TABLE 1: Contribution of heavy metal emissions from coal-fired public power plants to total emissions in the western part of Germany (Mirsal, 2008).

Pollutant	Contribution (wt%)	
	1982	**1990**
As	38	27
Cd	7	7
Cr	12	4
Cu	22	8
Hg	11	14
Ni	5	4
Pb	8	1
Se	1	1
Zn	7	6

Excessive emissions of trace metals, often in the form of particulates, contaminate the surface environment and also, as they become airborne, contribute to air pollution. Contaminant-bearing particulates in the atmosphere can be deposited on the Earth's surface, and then they may be re-suspended to re-enter the atmosphere (Nurdan S.,

2007). The emission of pollutants to the atmosphere often involves the direct uncontrolled exposure of large populations to toxic substances. This is especially relevant to urban areas, where the proximity between humans and pollutants is closet Nasr Yousef M. J. Omar *et.al.*, (2007).

Pb is a widely distributed and non-biodegradable toxic metal in the environment. It has been added to petrol since 1920s as an anti-knocking agent, to improve fuel efficiency and to reduce wear on vehicle engines. Leaded petrol has caused more environmental lead exposure than any other sources. (Landrigan, 2002; Amit Kumar Singh *et.al.*, 2006). Sources of Zn and Cd are from car components, tyre abrasion, lubricants, industrial and incinerator emissions. The source of Ni and Cr in street dust is believed to be corrosion of cars and chrome plating of some motor vehicle parts (Achilleas Christoforidis *et. al.*, 2009). Emission form road traffic occur at ground level along the streets in the most densely populated parts of the cities. They are due to wear brakes, tires, other vehicle components, road pavement and also due to exhaust emissions (Christer Johansson *et.al.*, 2008).

The major external source of heavy metal in soils is usually pollution caused by anthropogenic activities, such as metal mining, smelting, and processing. Additionally, diffuse pollution by wet and dry deposition has resulted in the long-term accumulation of heavy metals all over the world (Nowack *et al.*, 2001). Human activities such as metal mining, smelting and finishing, coal combustion, refuse incineration, burning of fossil fuels, and agriculture have greatly increased the fluxes of trace metals to aquatic environment (Nriagu and Pacyna, 1988; Pacyna, Scholtz, and Li, 1995; Rodrigues and Foormoso, 2006; Settle and Paterson, 1980; Han *et al.*, 2006). The urban environment is affected bu a wide variety of anthropogenic activities. Road networks, housing and the metal processing and manufacturing industries will tend to increase the heavy metal contect of soils (Rodrigues *et al.*, 1982; Davies and Thornton, 1987; Davies, 1990; J. Kelly *et al.*, 1996). This summarize that the influence of anthropogenic activities of heavy metals does not effect to on land environment, but also in aquatic environment; either direct or indirect effect of anthropogenic activities.

The main mechanism of heavy metal dispersion in the environment is atmospheric transport, anthropogenic Pb contamination is widely distributed (Lima *et al.*, 2005; Planchon *et al.*, 2002; Renberg *et al.*, 1994; Han *et al.*, 2006) and has detected in remote ares, including polar ice caps (Hong, Candelone, Patterson and Boutron, 1994), remote ponds (Shirahana, Elias, Patterson and Koide, 1980; Han *et al.*, 2006). Given the remote location of the Swiss national Park, which had been kept free form direct human impacts, except for hiking on a few trails since the beginning of the century, speculations were raised that the high metal contents may have resulted from the deposition of aerosols originating from the industrial centers of Northern Italy (Scheurer *et al.*, 1993; Bernd Nowack *et al.*, 2001). In southern Norway showed that atmospheric long-distance transport may indeed lead to heavy metal pollution of areas far away form large industrial and urban centers (Steinnes *et al.*, 1989; Nowack *et al.* 2001). Atmospheric pollution of soil is also increasing in Malaysia as urbanization and industrialization proceeds, yet few data are available to assess the impact and extent of the pollution (Zarcinas *et al.*, 2003).

The contamination of agricultural soils and crops by heavy metals is causing concerns due to the potential effect on human health and the possible long-term sustainability of food production in contaminated areas (Zarcinas *et al.*, 2003). The incidence of heavy metal contamination form both natural and anthropogenic sources has increased concern about the health effects of chronic low-level exposures, particularly people living in urban environment who are more likely to be exposed to this tread (Tahir *et al.*, 2007). Urban runoffs not only degrade the environmental quality of aquatic ecosystems, but also lead to increasing contaminants in aquatic organisms through bioaccumulation and biomagnifications, potentially causing elevated trace m,etal concentration in the food chain. Thus, once trace metals are emitted, they may remain in the environment and the food chain for a very long time (Nurdan S., 2007). T low levels, haem synthesis as well as psychological and neuro-behavioural functions is impaired. A high level of Pb exposure damages almost all organs and system, kidneys and blood, culminating in desth at excessive levels. It is of special concern to pregnant women as it acts as an abortifacient. The nervous system of the foctus is especially susceptible to Pb, which can cross the placenta and penetrate the blood-brain barrier. In children, the most

frequent results of Pb intoxication are irreversible damage to brain and the hindrance of body defense mechanisms (Amit Kumar Sigh *et. al.*, 2006). This shows that, exposure of heavy metals can occur through drinking water, food, air, soil and dust. Some of heavy metals occurred as by-product of metal processes or mining industry that exposed to environment. Children, especially toddlers, can easily ingest soils or indoor dust unintentionally when they put contaminated toys in their mouth, pick up foods with dirty hands, thus making them susceptible to toxic metals poisoning. In addition, adults may also be exposed to similar threat since inhalation is the most common pathway for toxic metals to enter inside human body (Tahir *et al.*, 2007).

CHAPETR 3

METHODOLOGY

3.1 SAMPLING LOCATION

For this study, the sampling area is determined around Ipoh until Bota area. This particular area have many industrial area such as Batu Gajah Industrial Area, Pengkalan Industrial Area and Bukit Merah Industrial Area. The purpose of choosing this industrial area is because to make a comparison between those industrial areas that has differences of industry activity. For example, Bukit Merah Industrial Area has several chemical industry activities such as Malay-Sino Chemical Industries Sdn. Bhd. that producing brine solution. For non-industrial area, the samples are taken from Taman Universiti Housing Area and Bota Rural area.

TABLE 2: Sampling Area.

Sampling Area	
Industrial Area	Non-industrial Area
Batu Gajah Industrial Area	Taman Universiti Housing Area
Pengkalan Industrial Area	Bota Rural Area
Bukit Merah Industrial Area	

For industrial areas.

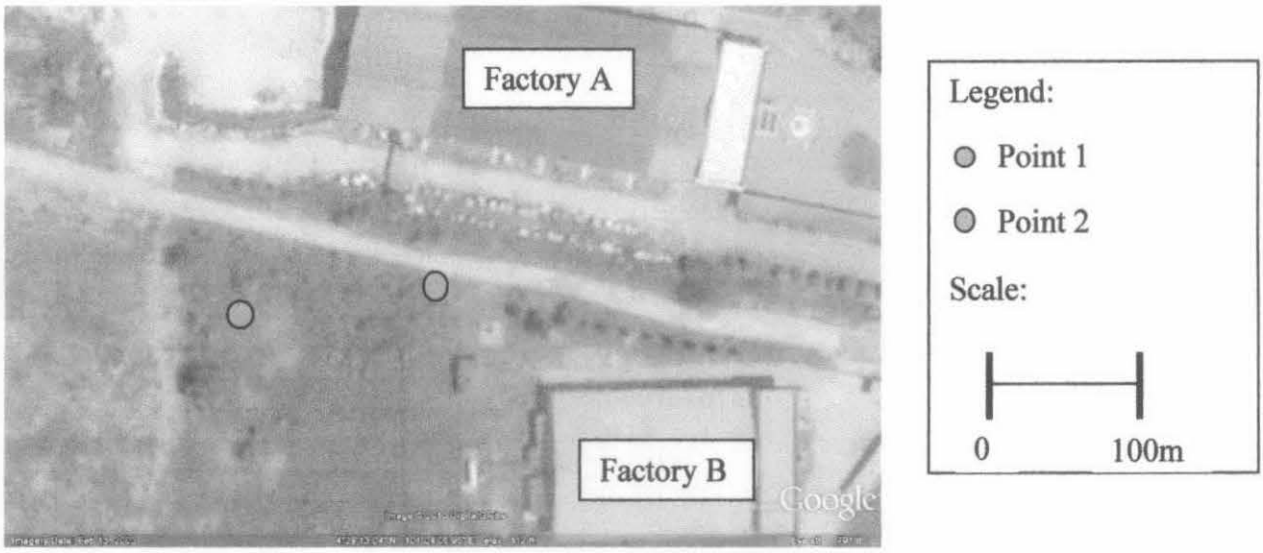

Figure 1: Sample point for industrial area at Batu Gajah (Source from Google Earth).

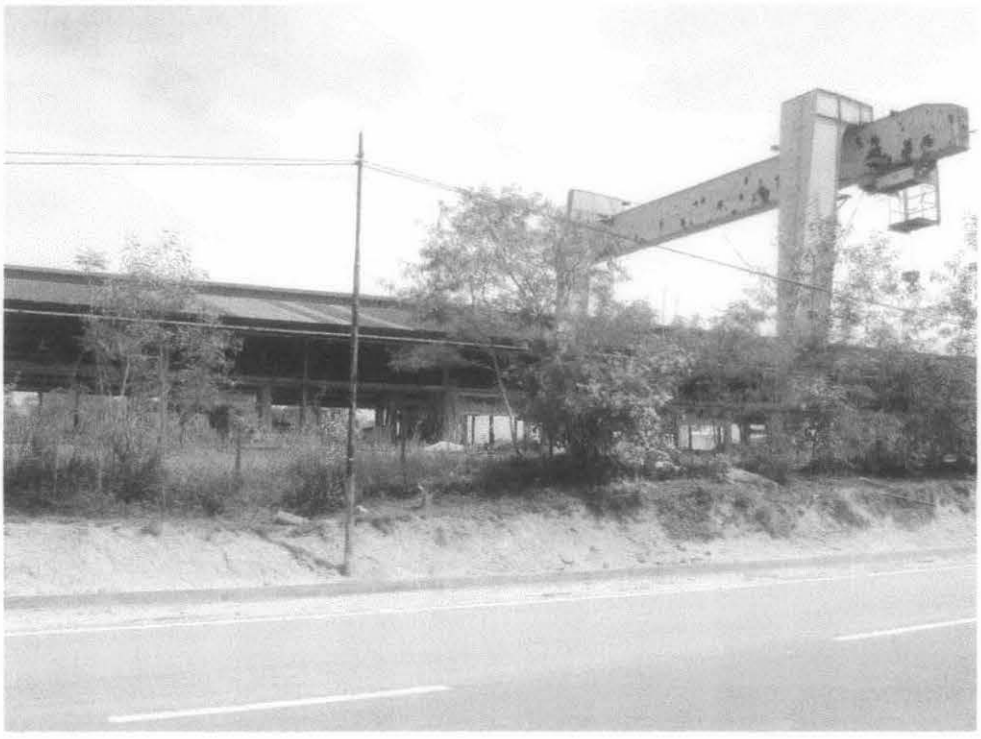

Figure 2: View of Factory A at Batu Gajah Industrial

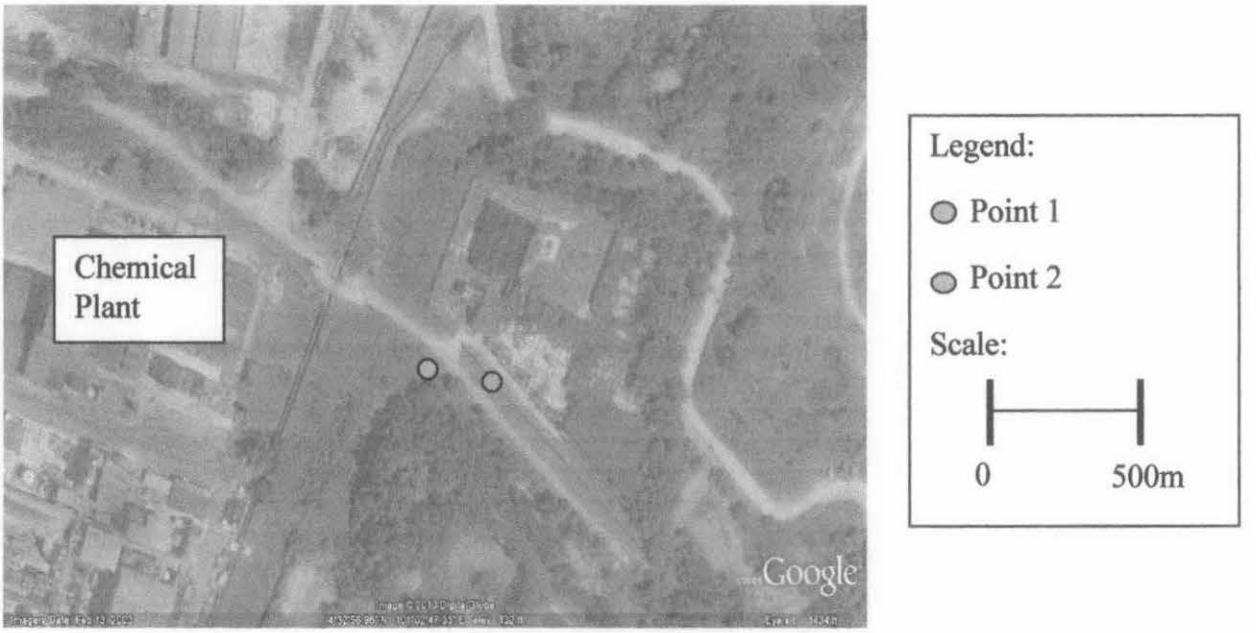

Figure 3: Sample point for industrial area at Bukit Merah (Source from Google Earth).

Figure 4: View of Chemical Plant at Bukit Merah Industrial Area.

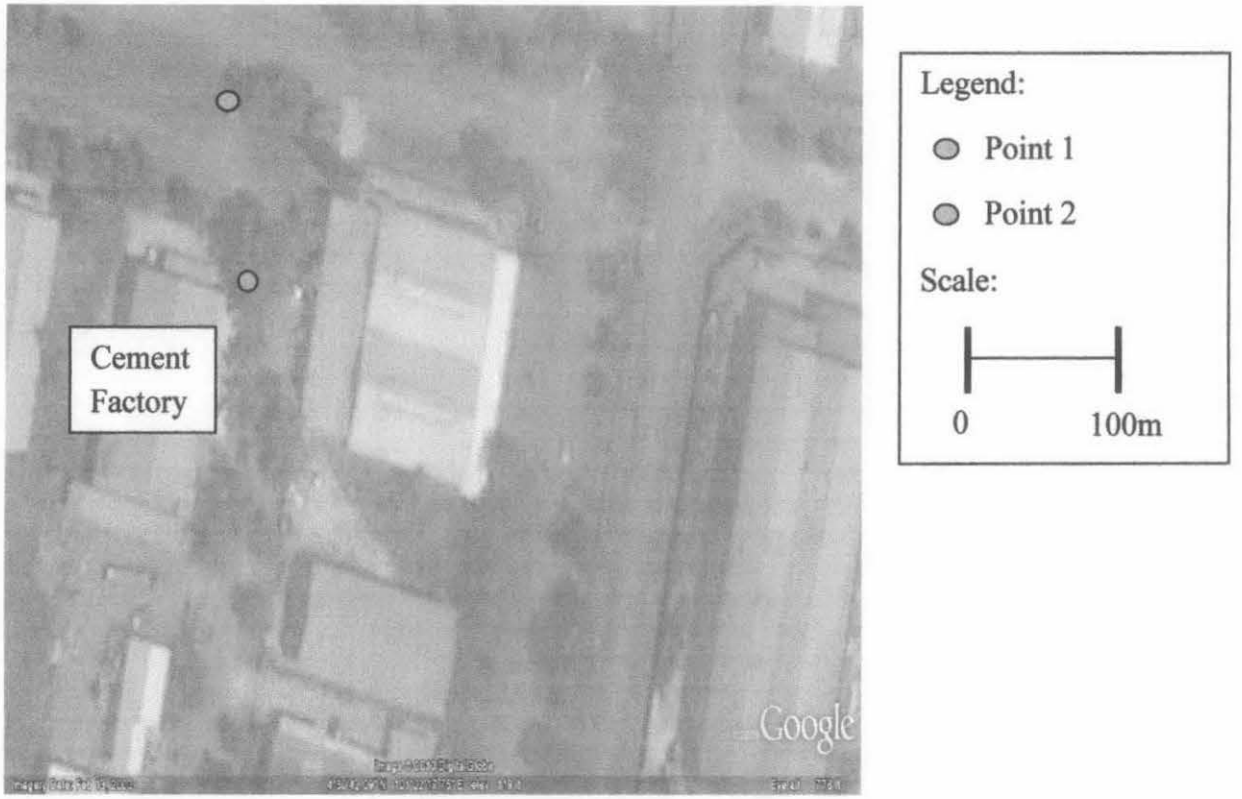

Figure 5: Sample point for industrial area at Pengkalan (Source from Google Earth).

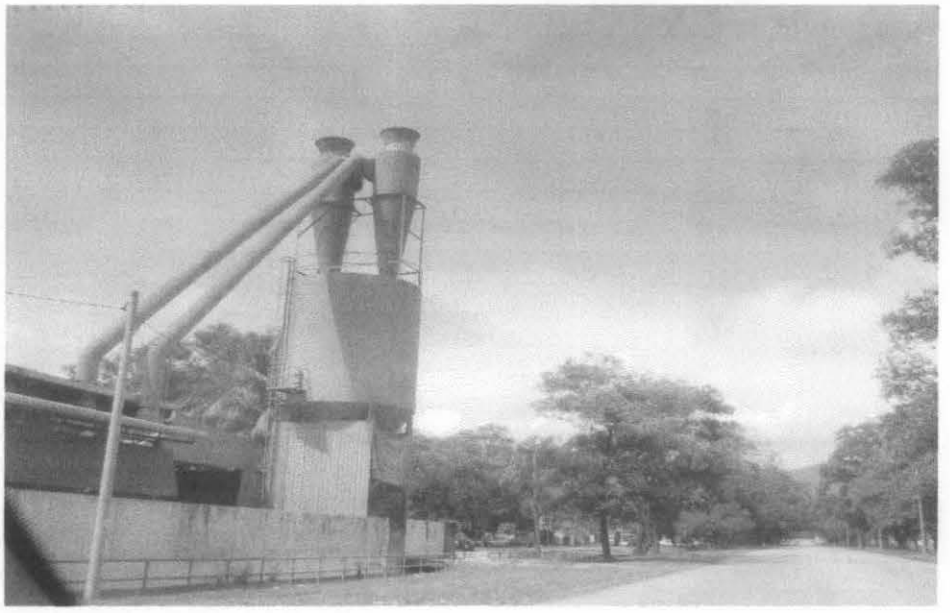

Figure 6: View of Cement Factory at Pengkalan Industrial Area.

For non-industrial areas.

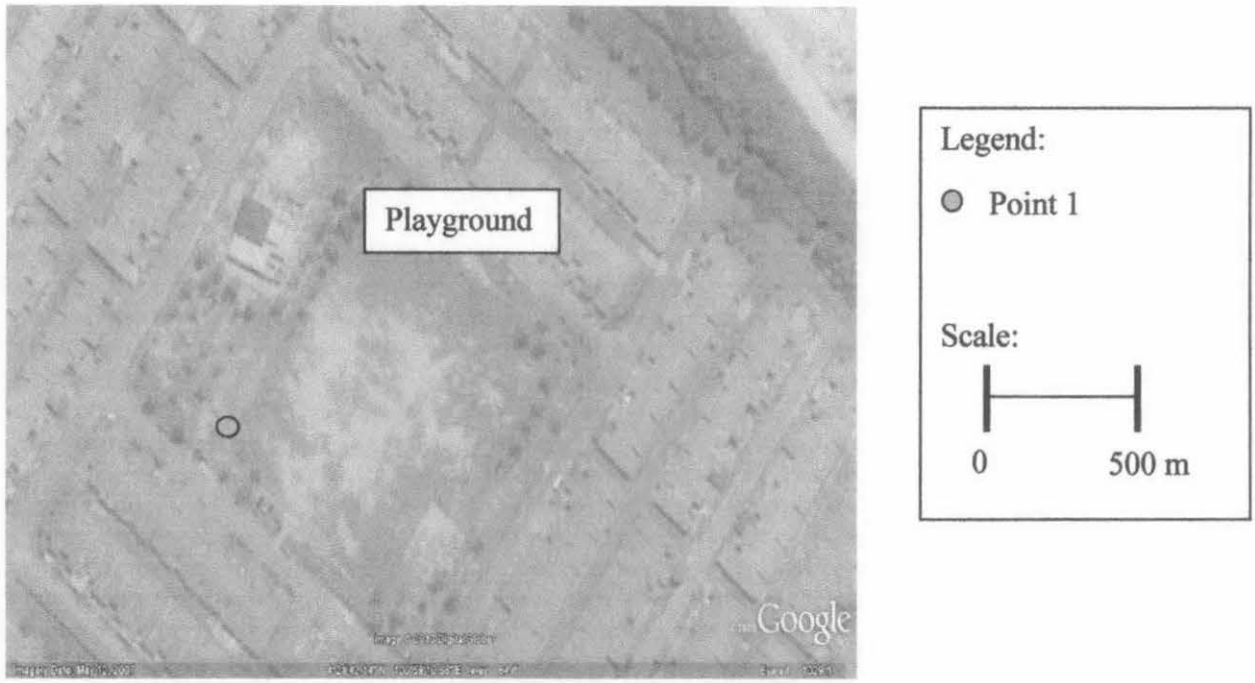

Figure 7: Sample point in Taman Univeristi, Bandar Seri Iskandar, Tronoh , Perak (Source from Google Earth).

Figure 8: View of playground at Taman Universiti Housing Area.

Legend:

Point 1

Point 2

Scale:

0 1000 m

Figure 9: Sample point in Bota Kanan , Perak (Source from Google Earth).

3.2 SAMPLING METHOD

1. For industrial area, the sampling area marked using 4 small sticks that arranged in square with length of 15-cm x 15-cm.

Figure 10: Sample collecting in Taman Universiti

2. By using gardening hand tool, the sample collected with the depth of soil around 2- 5cm.

Figure 11: Depth of soil sample during sample collecting in Taman Universiti

3. The soil sample kept in the plastic bag and labeled with A1 and A2 for Batu Gajah Industrial Area, B1 and B2 for Pengkalan Industrial Area and C1 and C2 for Bukit Merah Industrial Area.
4. For non-industrial area, procedure 1 to 3 repeated and soil sample labeled with D1 and D2 for Taman Universiti Housing Area and E1 and E2 for Bota Rural Area.
5. 2 samples are taken form each sample point.
6. All 10 samples are kept in laboratory for experimental work.

3.3 EXPERIMENTAL WORK

3.3.1 Preparation of soil samples

1. All 10 samples are weighted sample by sample and the readings are recorded.
2. All 10 samples are cleaned from organic matter such as grasses and plant root the weighted again before air-dried for three days then take the weight of each sample and the reading recorded.

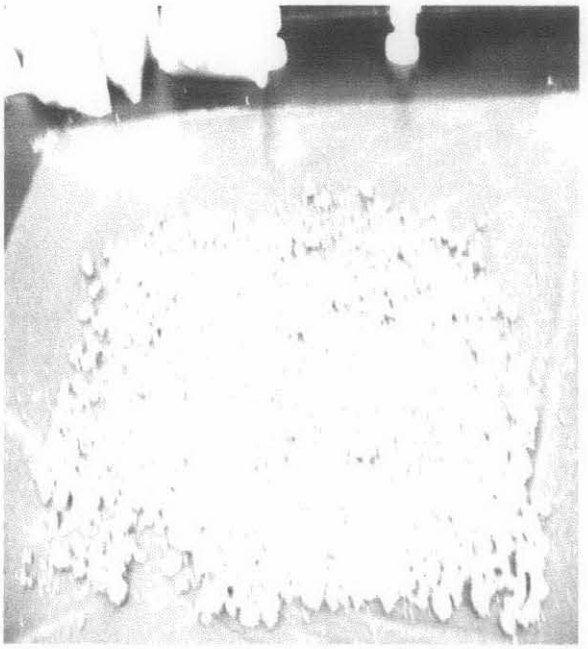

Figure 12: Sample air-dried for three days.

3. After air-dry, all samples is crushed and small amount of each sample with weight around 80 – 100g is taken form bulk sample and placed into an aluminum foil for heating over night.

Figure 13: Drying in oven overnight.

4. Each sample is sieved pass through a 1-mm sieve.
5. After sieving, all samples are placed in air-tight container for aqua regia digestion samples.

3.3.2 Digesting samples

The conventional aqua regia digestion procedure consists of digesting soil samples on a hot plate with 3:1 mixture of HCl and HNO_3 (Chen *et al.*, 2001; Nieuwenhuize *et al.*, 1991). The procedure of aqua regia digestion is as followed:

1. 0.5g of sample A1 is weighted and placed in a 100ml of beaker.
2. 12ml of aqua regia is put into a 0.5g sample of Sample A1 that placed in a 100ml of beaker.
3. A watch glass is placed on the top of 100ml of beaker.

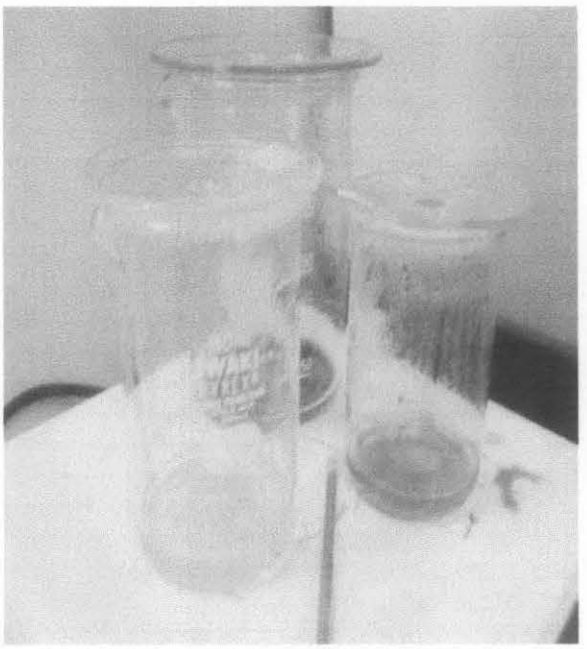

Figure 14: Aqua regia digestion.

4. A hot plate temperature is setted to 110°C.
5. After the temperature of hot plate reach to 110°C, a beaker that has Sample A1 and aqua regia is placed on the top of hot plate for 3 hours.
6. After 3 hours, 20ml of nitric acid (2% v/v H_2O) is added to a solution of Sample A1 and let the solution to cool in room temperature.

7. After cooling in room temperature, the solution of Sample A1 is filtered and diluted using dionized distilled water (DDW) in a volumetric flask of 100ml.

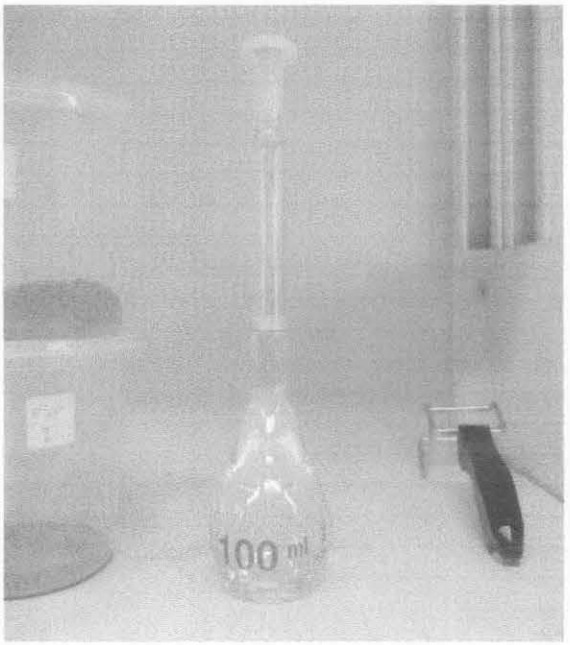

Figure 15: 100ml diluted sample solution.

3.3.3 Measuring pH of soil samples.

The pH values will indicates level of the organic matter that content in soil sample which gives the view of level of contamination of each sample soil. It will be a reference for this study to relate the pH value with level of concentration of heavy metals on soils.

1. 100 g of raw sample soil of A1 is placed inside a 250 ml beaker.
2. 200ml of dionized distilled water (DDW) is mixed with A1 raw soil sample.
3. The mixture of raw soil sample of A1 is centrifuged to ensure well-balance mixing within raw soil sample and DDW for 5 minutes.
4. pH value of soil sample is determined by using pH meter.
5. All reading is recorded.
6. Step 1 until 6 is repeated for sample A2, B1, B2, C1, C2, D1, D2, E1 and E2.

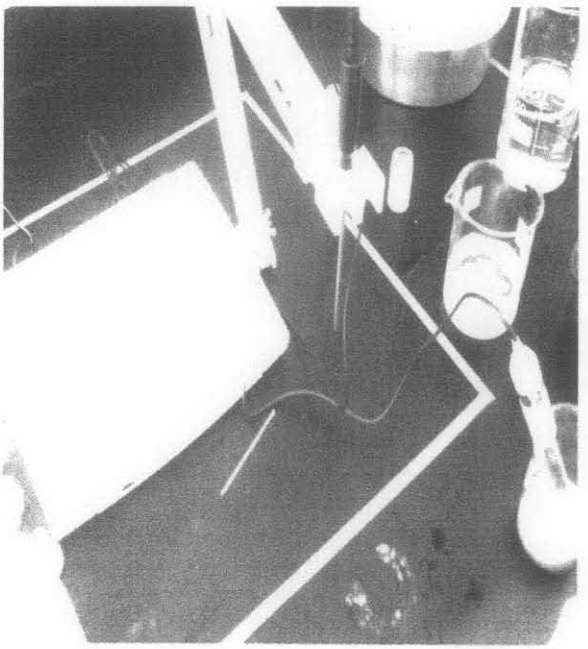

Figure 16: Measuring pH value of soil sample.

3.3.4 Atomic Absorption Spectroscopy (AAS) Theory and Principles

According to Tom Huff (1998), Atomic Absorption Spectroscopy (AAS) determines the presence of metals in liquid sample. It also measures the concentration of metals in the samples. It is typical concentration range is in the low range of ppm or mg/L.

In their elemental form, metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interest is aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. As concentration goes up, absorbance goes up. The researcher can construct a calibration curve by running standards of various concentrations on the AAS and observing the absorbances. In this lab, the computer data system will draw the curve. Then samples can be tested and measured against this curve.

In atomic absorption, there are two methods of adding thermal energy to a sample. A graphite furnace AAS uses a graphite tube with a strong electric current to heat the sample. In flame AAS, we aspirate a sample into a flame using a nebulizer. The flame is lined up in a beam of light of the appropriate wavelength. The flame (thermal energy) causes the atom to undergo a transition from the ground state to the first excited state. When the atoms make their transition, they absorb some of the light from the beam. The light beam is generated by a lamp that is specific for a target metal. The lamp must be perfectly aligned so the beam crosses the hottest part of the flame and travels into the detector. The detector measures the intensity of the beam of light. When some of the light is absorbed by a metal, the beam's intensity is reduced. The detector records that reduction as absorption. That absorption is shown on a readout by the data system. As the diagram indicates in **Figure 17**, there are four primary parts to the system--the light source, the flame apparatus, the detector, and the data system.

The instrument will record the absorption generated by a given concentration. By plotting the absorption versus the concentrations of the standards, a calibration curve can be plotted.

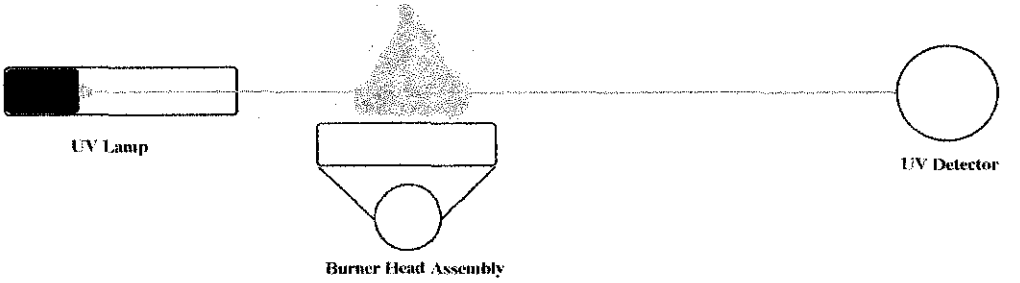

Figure 17: The schematic diagram of a flame AAS.

CHAPETR 4

RESULT AND DISCUSSION

4.1 RESULT

Based on Zarcinas *et al.* (2003), the concentration of heavy metals on soils is compared with Dutch Standard and Australian Ecological Investigation Levels (EIL) in mg/kg.

Table 3: Dutch target values and Australian EIL (Zarcinas *et al.*, 2003).

Metal	Dutch target value	Australian EIL
Pb	85	600
Ni	35	60
Zn	140	200
Cd	0.8	3
Cr	100	400

The Dutch target values are based on natural soil levels and on negligible risk concentration. Usually, Dutch Standard gives the lowest concentration value that can be uses in this study compare with Australian EIL, the concentration values are too high and in result, all concentration heavy metals value in this study will be classified as below detection limit.

For AAS analysis result are shown below:

Table 4: Concentration of Pb in soils

Sample	1st Replication	2nd Replication	Average	mg/kg
A1	1.4761	1.7550	1.6155	323.0
A2	2.5916	2.0339	2.3127	462.54
B1	1.5159	2.2331	1.8745	374.90
B2	1.4761	1.7550	1.6155	323.10
C1	1.9143	1.6753	1.7948	358.96
C2	1.9143	1.7151	1.8147	362.94
D1	1.8347	1.9542	1.8944	378.88
D2	2.0737	1.9542	2.0139	402.78
E1	1.5558	1.3167	1.4362	287.24
E2	2.1135	2.0737	2.0936	418.72

Legend:

A1 = Batu Gajah Industrial Area
A2 = Batu Gajah Industrial Area
B1 = Pengkalan Industrial Area
B2 = Pengkalan Industrial Area
C1 = Bukit Merah Industrial Area
C2 = Bukit Merah Industrial Area
D1 = Taman Universiti
D2 = Taman Universiti
E1 = Bota Kanan
E2 = Bota Kanan

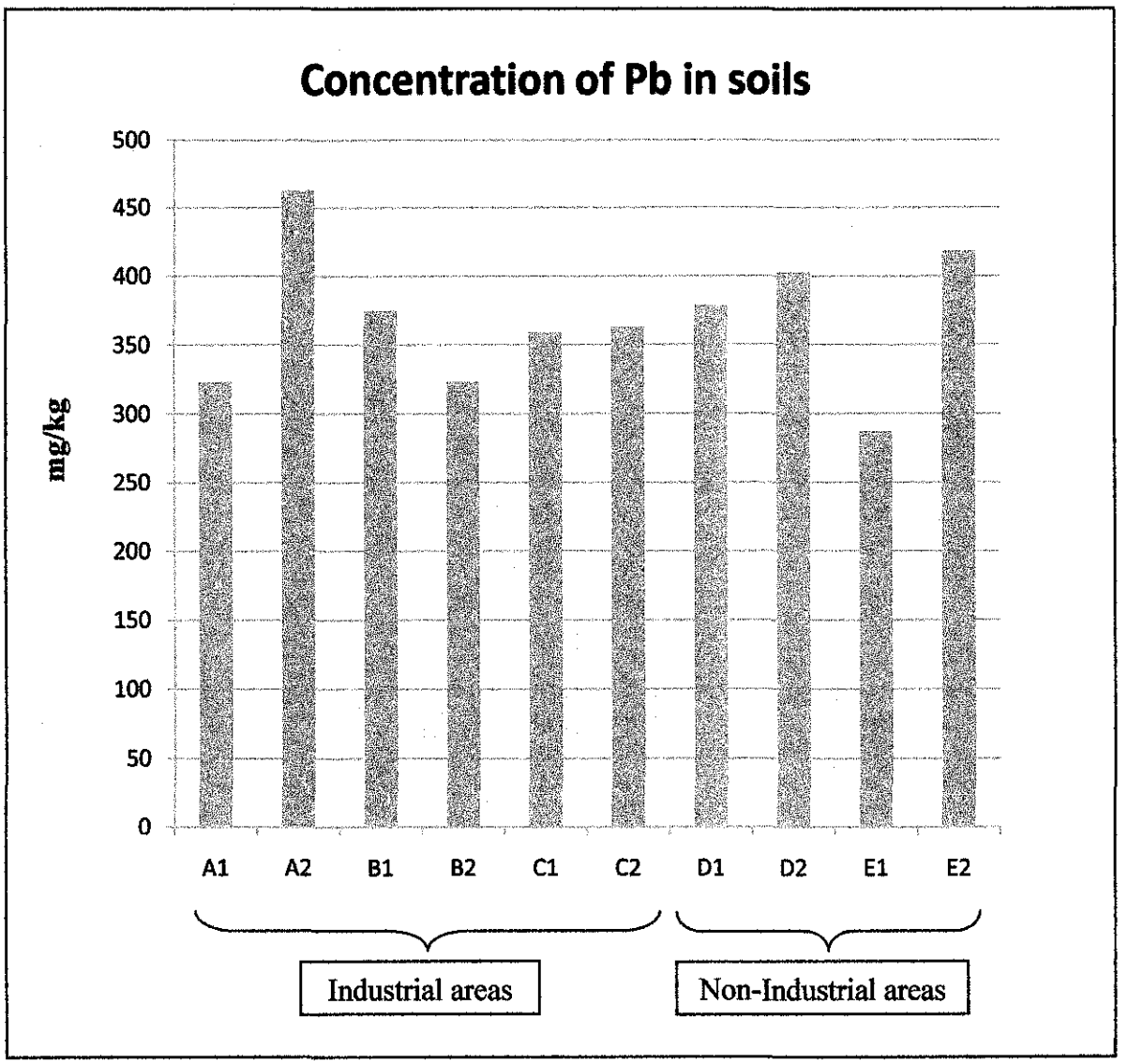

Figure 18: Concentration of Pb in soils at industrial and non-industrial areas.

The highest concentration of Pb is 462.54 mg/kg which is at Batu Gajah Industrial Area point 2 and the lowest is 287.24 mg/kg which is at E1 which represents non-industrial area at Bota Kanan point 1. The range concentration of Pb is between 287 to 462 mg/kg for both areas.

Table 5: Concentration of Ni in soils.

Sample	1st Replication	2nd Replication	Average	mg/kg
A1	0.1917	0.2122	0.2019	-
A2	0.1653	0.1770	0.1711	-
B1	0.1565	0.1360	0.1462	-
B2	0.1419	0.1653	0.1536	-
C1	0.8420	0.6633	0.7526	150.52
C2	0.2151	0.1712	0.1931	-
D1	0.1477	0.1858	0.1667	-
D2	0.1624	0.1360	0.1492	-
E1	0.1799	0.1682	0.1740	-
E2	0.1917	0.1975	0.1946	-

Legend:

A1 = Batu Gajah Industrial Area
A2 = Batu Gajah Industrial Area
B1 = Pengkalan Industrial Area
B2 = Pengkalan Industrial Area
C1 = Bukit Merah Industrial Area
C2 = Bukit Merah Industrial Area
D1 = Taman Universiti
D2 = Taman Universiti
E1 = Bota Kanan
E2 = Bota Kanan

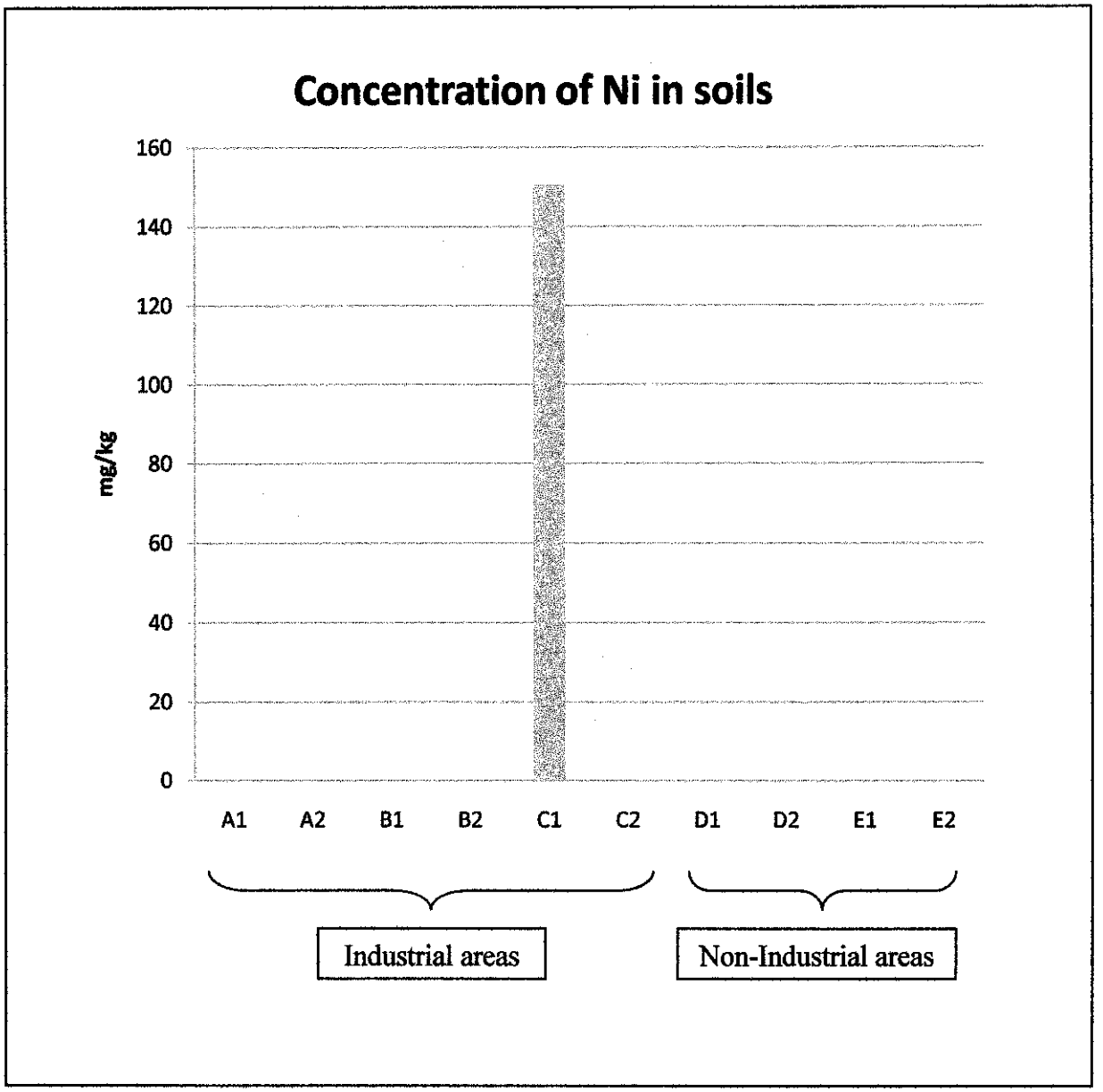

Figure19: Concentration of Ni in soils at industrial and non-industrial areas.

Ni only presence at C1 which is Bukit Merah Industrial Area with the concentration of Ni is 150.52 mg/kg. For the other area, Ni was not detected.

Table 6: Concentration of Zn in soils.

Sample	1st Replication	2nd Replication	Average	mg/kg
A1	0.0072	0.1542	0.1542	154.20
A2	0.0085	0.1563	0.1563	156.30
B1	0.0503	0.2243	0.2243	224.30
B2	0.0194	0.1740	0.1740	174.00
C1	0.0074	0.1545	0.1545	154.50
C2	0.0134	0.1643	0.1643	164.30
D1	0.0102	0.1591	0.1591	159.10
D2	0.0070	0.1539	0.1539	153.90
E1	0.0232	0.1802	0.1802	180.20
E2	0.0150	0.1669	0.1669	166.90

Legend:

A1 = Batu Gajah Industrial Area
A2 = Batu Gajah Industrial Area
B1 = Pengkalan Industrial Area
B2 = Pengkalan Industrial Area
C1 = Bukit Merah Industrial Area
C2 = Bukit Merah Industrial Area
D1 = Taman Universiti
D2 = Taman Universiti
E1 = Bota Kanan
E2 = Bota Kanan

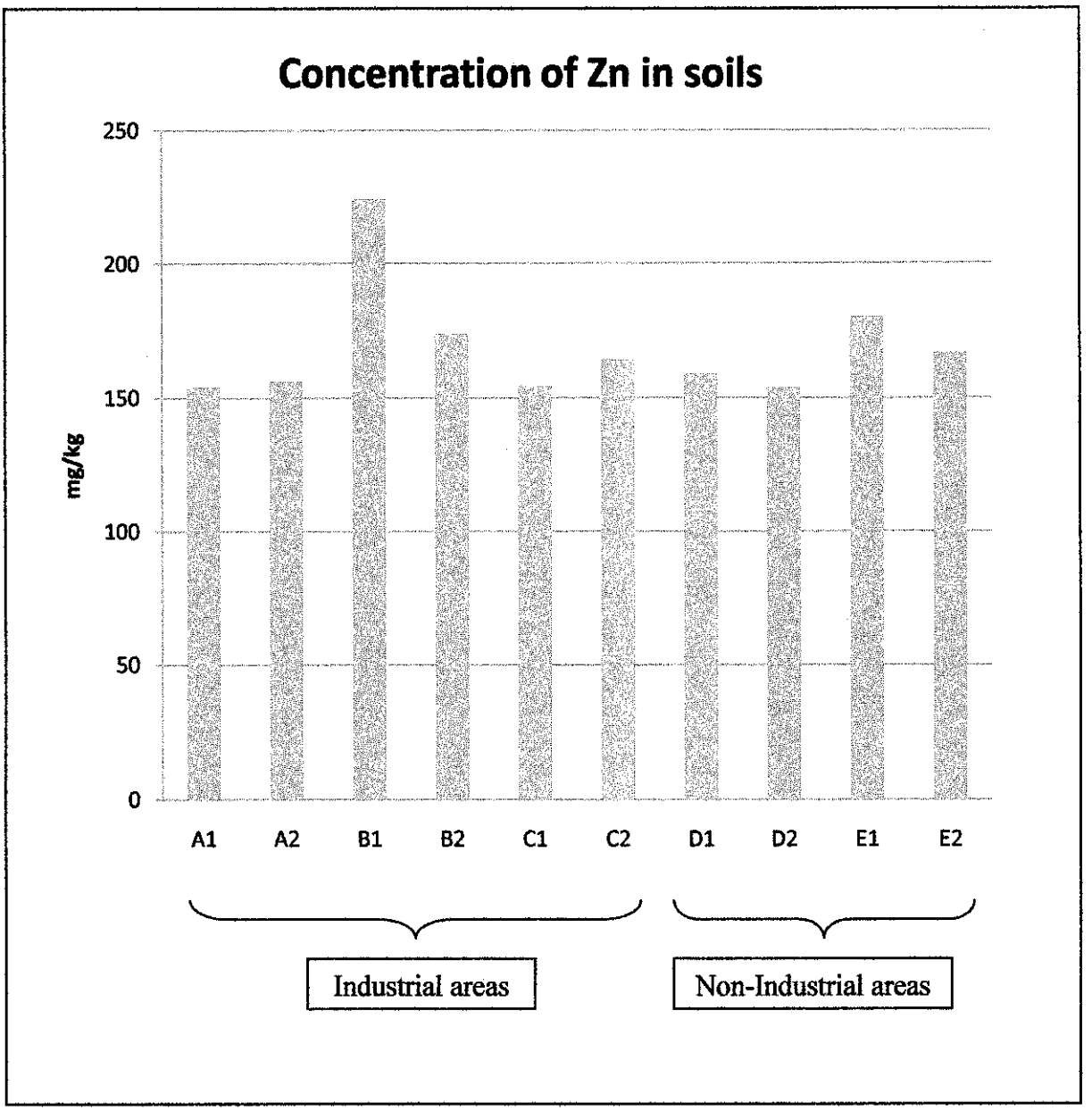

Figure 20: Concentration of Zn in soils at industrial and non-industrial areas.

The highest concentration of Zn is 224.30 mg/kg which is at Pengkalan Industrial Area point 1. The lowest Zn concentration is 153.90 mg/kg which is at Taman Universiti Housing Area point2. The range concentration of Zn is between 153 to 224 mg/kg for both areas.

Table 7: Concentration of Cd in soils.

Sample	1st Replication	2nd Replication	Average	mg/kg
A1	0.2769	0.2355	0.2562	51.24
A2	0.2322	0.2598	0.2460	49.20
B1	0.1124	0.1168	0.1146	22.92
B2	0.1223	0.1187	0.1205	24.10
C1	0.2114	0.1769	0.1942	38.84
C2	0.1998	0.1784	0.1891	37.82
D1	0.0621	0.0613	0.0617	-
D2	0.0691	0.0605	0.0648	-
E1	0.0699	0.0644	0.0672	-
E2	0.0706	0.0675	0.0691	-

Legend:

A1 = Batu Gajah Industrial Area
A2 = Batu Gajah Industrial Area
B1 = Pengkalan Industrial Area
B2 = Pengkalan Industrial Area
C1 = Bukit Merah Industrial Area
C2 = Bukit Merah Industrial Area
D1 = Taman Universiti
D2 = Taman Universiti
E1 = Bota Kanan
E2 = Bota Kanan

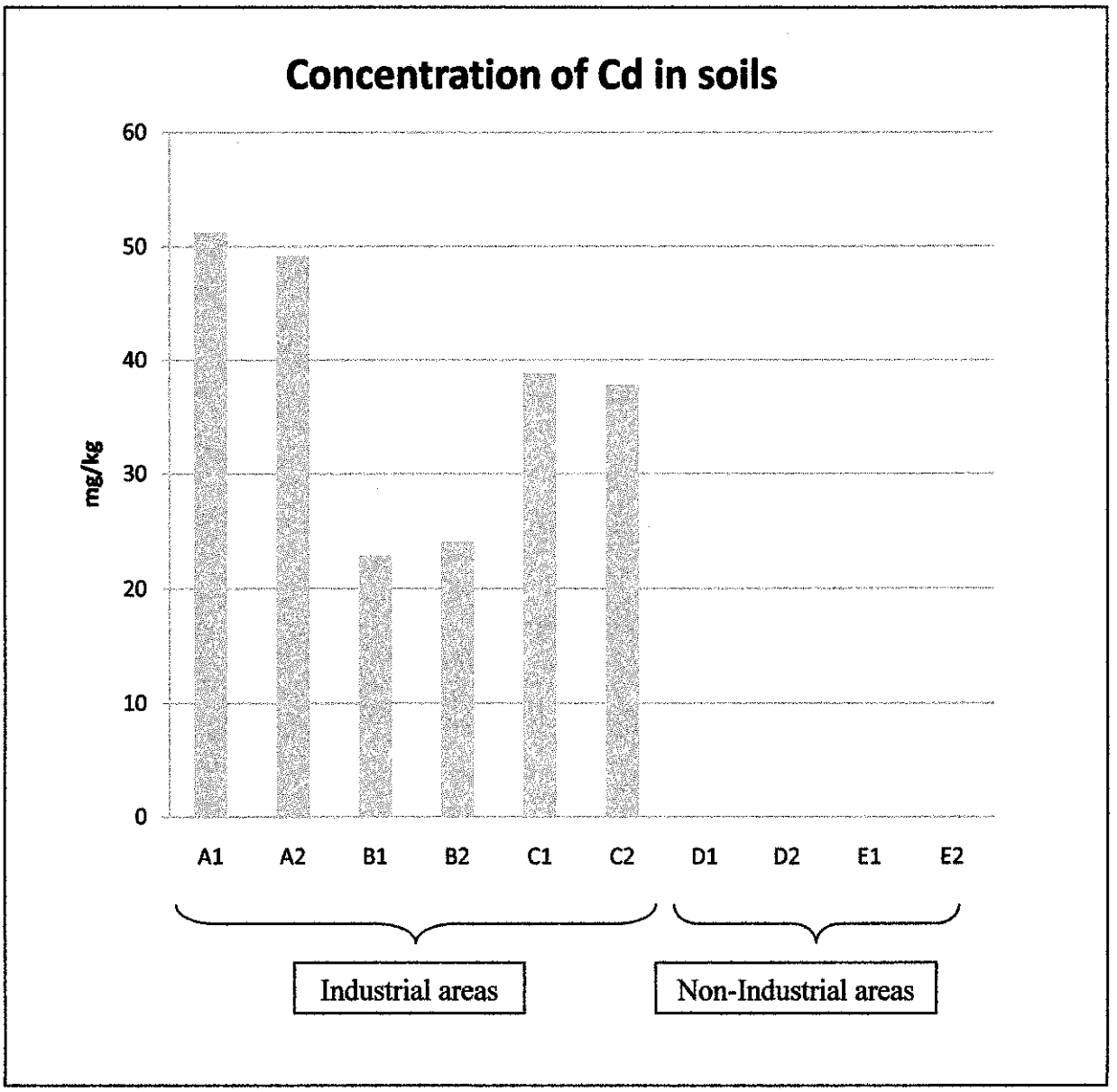

Figure 21: Concentration of Cd in soils at industrial and non-industrial areas.

The highest concentration of Cd is 51.24 mg/kg which is at A1 and the lowest is 22.92 mg/kg which is at B1. The range concentration of Cd is between 22 to 52 mg/kg for industrial area while at non-industrial area; there is no presence of Cd.

Table 8: Effect of Chromium (Cr) in soils between industrial and non-industrial areas.

Sample	1st Replication	2nd Replication	Average	mg/kg
Industrial	0.4189	0.4065	0.4127	82.54
Non-industrial	0.2703	0.2517	0.2610	52.20

For industrial area, the reference soil sample is from Bukit Merah Industrial Area. In Bukit Merah Industrial Area, most of industry activity is more into a chemical manufacturing product processes. Moreover, the density of industry actovoty is high as compare to Pengkalan Industial Area and Batu Gajah Industrial Area. Thus, these make more significant result of the impact of industrial activity to environment. However, for non-industrial area, Bota Rural Area is chosen as a reference soil sample point. It is because, Bota Rural Area is the area that not under the influence of development activity. Compare to Taman Universiti Haousing Area, the housing area is the re-development area that previously the ex-mines area is transformed into a housing area. Even though the ex-mines area already change into housing area, the effect of heavy metal is still occurs in soils and take long time to decompose the heavy metal in soils. For Bota Rural Area, it is an area that un0disturb area and only small human activities such as agriculture. Most of people in Bota Area are farmers.

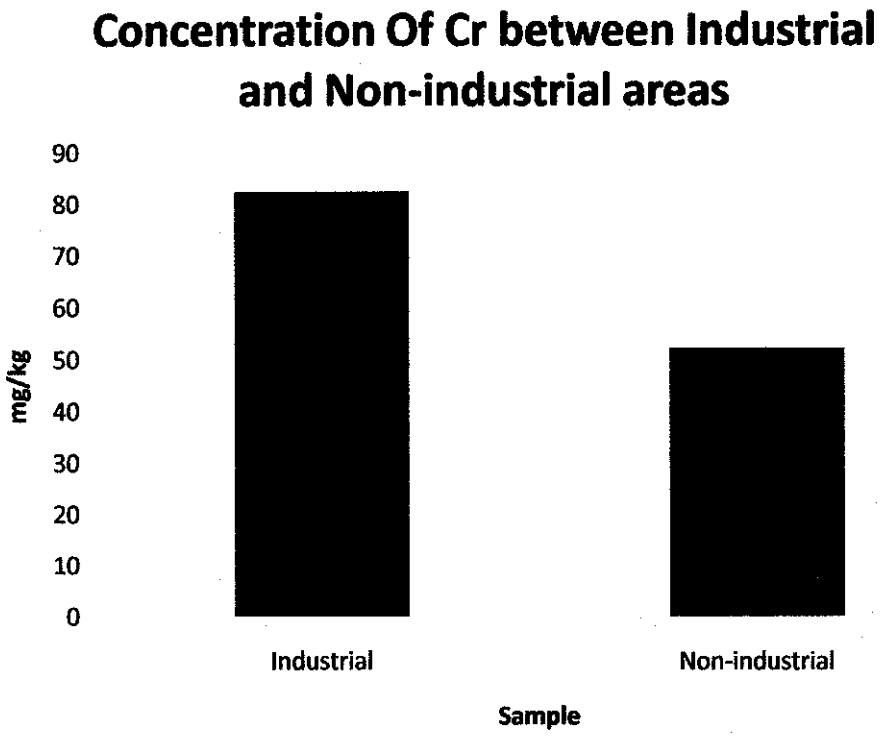

Figure 22: Concentration of Cr in soils between industrial and non-industrial areas.

The highest concentration of Cr is 83 mg/kg which is at industrial area and the lowest is 52 mg/kg which is at non-industrial area. This graph shows the effect of industrial activity by emission of heavy metal into the atmosphere. It is shows that industrial area gives high value of concentration of Cr in atmosphere compare to non-industrial area.

Table 9: pH value for each soil sample

Sample	pH value
A1	7.26
A2	5.55
B1	5.24
B2	5.48
C1	4.95
C2	5.63
D1	4.65
D2	4.64
E1	5.95
E2	4.66

Legend:

A1 = Batu Gajah Industrial Area
A2 = Batu Gajah Industrial Area
B1 = Pengkalan Industrial Area
B2 = Pengkalan Industrial Area
C1 = Bukit Merah Industrial Area
C2 = Bukit Merah Industrial Area
D1 = Taman Universiti
D2 = Taman Universiti
E1 = Bota Kanan
E2 = Bota Kanan

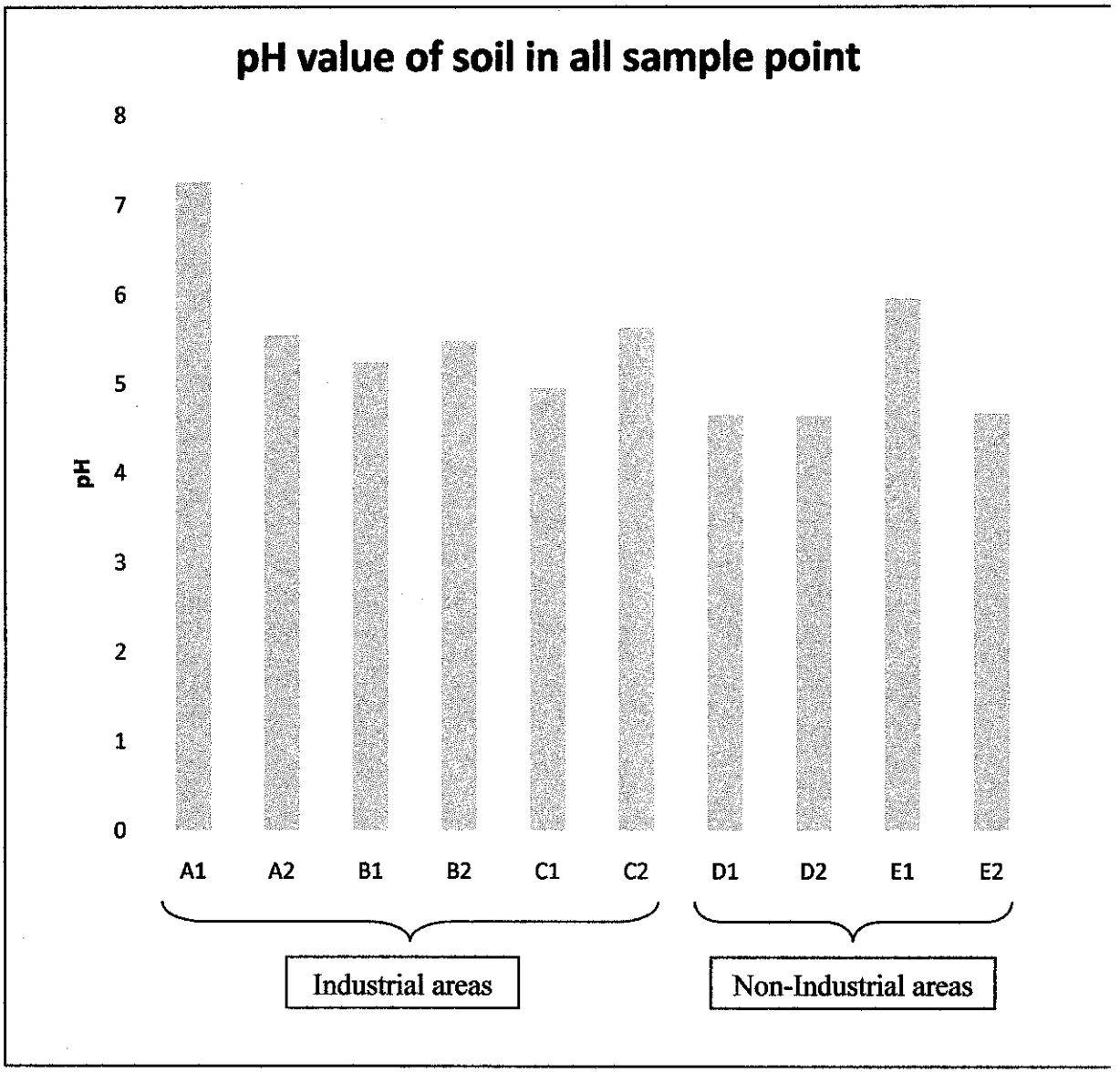

Figure 23: pH value of soils in all sample points.

The most acidic soils are at D2 and the neutral pH of soils is at A1. Most of soils pH is acidic characteristic which is below than pH of 6 and only one soil sample that exceed pH of 6 which is point A1.

4.2 DISCUSSION

The concentrations of Pb at industrial and non-industrial areas are found at range between 287 to 462 mg/kg. The highest concentration is found at A2 which is at Batu Gajah Industrial area. The lowest concentration is found at E1 which is at Bota Kanan. For overall, the concentration of Pb does not show much difference and it is difficult to differentiate the effect of anthropogenic activities at both areas. It is because Pb is common heavy metal at both areas. This may reflect the effect of vehicular activity; that is the usage of leaded petrol or gasoline in Malaysia which already banned since late 90's. For industrial areas, the concentration of Pb is high because of high traffic density in industrial area and also the effect of emission. For non-industrial areas, which are point D1, D2, E1 and E2, where the sample taken from Taman Universiti and Bota Kanan respectively, the effect of vehicular is the main source of emission of heavy metal in the atmosphere. Especially at Taman Universiti, which is a newly re-developed areas from mining activities and until now, there still development made in Taman Universiti for housing purposes, the traffic density still high and may cause the high emission of heavy metal such as Pb from vehicular activity and re-development activity in that area.

The concentration of Ni was only found at point C1 which is Bukit Merah Industrial area. The concentration of Ni in that area is 150.52 mg/kg. Besides point C1, probably Ni was undetectable in other areas. The reason why only point C1 show the present of Ni is probably because the heavy metal is transported by wet deposition, where during sample collection, point C1 was wet and the weather of sample collected at point C1 was after the rain. Point C2 is located near to point C1 but separate at a road and C2 is nearer to a lake. Therefore, the presence of Ni at point C2 is already transported into the lake nearby.

The concentrations of Zn are found to be in range of 153 to 224 mg/kg. The highest concentration is found at B1 which is at Pengkalan Industrial area. The lowest concentration is found at D2 which is at Taman Universiti. The concentration of Zn is almost related to Pb because both heavy metals show difficulty to differentiate the

effect of anthropogenic at both areas. Zn and Pb are the heavy metal that related to vehicular activity. For point A1, A2, D1 and D1, the concentration of Zn is almost similar. This gives an observation that there are no significant differences at industrial and non-industrial areas. This is probably because; the atmospheric emission from industrial activity is not a factor that affects the concentration of Zn in soils. The vehicular activity or traffic density contributes toward the transportation of Zn into the environment.

For Cd, the concentrations are found in a range of 22 to 52 mg/kg. Cd is found only at industrial area and this gives a significant difference towards the effect of anthropogenic of heavy metal towards environment. The highest concentration of Cd is at Batu Gajah Industrial Area, followed by Bukit Merah Industrial Area and lastly Pengkalan Industrial Area. Also, the presence of Cr in industrial area and non-industrial show the impact of industrial activity toward environment. In industrial area, the concentration of Cr is to be found 82 mg/kg which is higher that the concentration in non-industrial area. The industrial activities may probably give a significant impact of heavy metals in atmosphere that accumulated in emissions of industry.

For non-industrial areas, soil pH in points D1 and D2 is more acidic and both are sample point at Taman Universiti which is 4.65 and 4.64 respectively. Meanwhile, at Bota Kanan which is point E1 and E2, the range of pH are 5.95 and 4.66 respectively. pH of soils are generally cause by the organic mater content in soils which is related to the capability of soils to support the life living in. pH of soils also give an effect of mobility of heavy metal in soils where the heavy metal already deposited form the atmosphere into the soils may be transported further. In industrial area, soils in point A1 gives the highest pH values where it is almost neutral compare to others industrial area that give acidic pH value. This shows that, soil at point A1 is less mobile than the other heavy metals.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Industrialization is one of the anthropogenic activities that gives effects towards the environment. The emission of industry is released into the atmosphere and content heavy metals which are then deposited by wet deposition or dry deposition into soils. Thus, soils are used as a medium to investigate the impact of industrial activity towards the environment. From this study, it was shown that Pb and Zn are the heavy metals that common in the atmosphere. It is because the concentrations of Pb and Zn are high in soils at industrial as well as non-industrial areas. Presence of Cd and Cr in soils shows the impact of industrial activity towards environment. It is because only at industrial areas show the presence of Cd. Meanwhile, for Cr, the industrial area gives higher concentration compare to non-industrial area. These could prove that industrial activity gives an impact to environment by releasing emissions into the atmosphere and increases the content of heavy metals into atmosphere.

For Pb and Zn, the concentrations for both areas are almost similar. It is because Pb and Zn are common heavy metal that is present in the atmosphere. These heavy metals are difficult to differentiate thus; it does not show a clear view of the impact of industrial activity towards the environment. The presence of Pb and Zn caused may be by other anthropogenic activities such as vehicular activities. The presence of Pb and Zn could be caused by the acceleration and stopping mechanism in the vehicle system.

5.2 RECOMMENDATION

For sampling collection, the purpose of digging the soil with the depth of 3cm is to determine the content of heavy metal at the surface of the soil or which is called topsoil. It is a constant parameter for all sampling location. In the methodology, it is stated that the depth of soil dug is 2cm, but in real sampling activity 3cm of depth is needed to take consideration of the thickness of growth such as grasses and plant roots. Pollution impact is higher when the distance of the sample point is closer to the source of industrial emission. To avoid the transportation of heavy metal by water, sample collection should be done during dry season.

For experimental work, it is recommended to make replication of sampling analysis to decreases the chances of an error result. A mean value of each sample is recorded. For this study, the sample will be analyzed 2 times and a mean value of each sample is recorded. For the digestion sample, it is recommended to prepare the more equipments and glassware more in laboratory. The equipment in laboratory such as hot plate heater must have a temperature controller that is easy to adjust the temperature to the exact required temperature for digestion which is 110°C.

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APPENDICES

WORK INSTRUCTIONS FOR ATOMIC ABSORPTION

A

Work Instructions For Atomic Absorption (AA-6650) Shimadzu

1. Type/Model of equipment: Shimadzu Atomic Absorption Spectrophotometer AA-6650.

2. Purpose: To present step by step operational instructions of Shimadzu Atomic Absorption Spectrophotometer AA-6650 to analyze samples for mineral determination.

3. Responsibility: Lab Incharge

4. Operational steps:

4.1 Switch ON ventilator.

4.2 Switch ON AA-6650 and press Buzzer OFF at the right side of the main unit. Wait for initialization until buzzer sound beeps three times.

4.3 Open acetylene gas cylinder anti-clock wise with key and set secondary gauge pressure at 0.09 MPa with pressure regulator (adjustment possible while purging; 4.5).

4.4 Switch ON Air compressor and confirm that secondary pressure gauge is set at 0.35 MPa.

Note: Open Drain Knob of air compressor tank until Pressure approaches zero then close it.

4.5 Press PURGE button of gas controller at the right side of the main unit and set the following readings on gauges.

Fuel = 0.07MPa

Oxidant = 0.25MPa

Flow = 8L/min

4.6 Confirm the DRAIN level bottle is filled with water.

4.7 Switch ON computer to the MS-Windows.

4.8. Double click on the icon of AA Software (WizAArd). The WizAArd Selection dialog box will appear on the screen.

4.8.1. WIZZARD SELECTION

4.8.1.1 Select the element selection ICON on the WizAArd sheet.

4.8.1.2 Click OK (or double click)

4.8.2. ELEMENT SELECTION

4.8.2.1 Click on the <Select Element>, load parameter will appear.

4.8.2.2 Click on the button and select the element symbol.

4.8.2.3 Click on the following;

- Flame
- Normal Lamp

4.8.2.4 Click OK.

4.8.2.5 Click EDIT PARAMETERS.

4.8.3. PARAMETERS:

4.8.3.1 Repeat measurement Conditions

4.8.3.2 Set number of repetitions (at least three) and Maximum number of repetitions by scrolling the digits (if different then parameters already in default).

4.8.4. WEIGHT CORRECTION FACTOR:

4.8.4.1 If required / as per procedure (Better to add individual entries on Analysis Chart).

4.8.5. CALIBRATION CURVE PARAMETERS

4.8.5.1 Concentration Unit ppm

4.8.5.2 Order 1st

4.8.5.3 Zero intercept "YES"

4.8.6 ANALYST

4.8.6.1 Name / Initials / Designation

4.9 Click OK.

4.10 Click NEXT.

4.11 Click EDIT on the sheet.

NOTE: For Standard Calibration Curve note number of Standards and their respective concentrations (as per guidance given Cook Book of AA).

4.12 Click NEXT.

4.12.1 SAMPLE ID

4.12.1.1 Give number of samples.

4.12.1.2 Enter sample ID (Sample Name) into the cell using key board.

4.12.1.3 Arrange your samples (entries are possible on data analysis sheet during operation).

4.13 Click NEXT.

4.13.1 CONNECT INSTRUMENT/ SEND PARAMETERS.

4.13.1.1 Check that power of AA-6650 is already ON.

4.13.1.2 Click on <Connect/Send parameters>.

4.13.1.3 Initialize dialogue box will open and AA main unit will start initializing.

4.13.1.4 Click OK, while a message appears on screen "Switch ON the Ventilator (as ventilator has been switched on earlier).

4.13.1.5 Press the EXTINGUISH button on the instrument (when message appear "Gas Leak Check will be started") & click OK on PC screen simultaneously.

NOTE: Gas leak check will start and will take 11 minutes (a small window in right down corner of window will show its status).

After 11minutes, message will appear on screen "No Gas Leakage Detected".

NOTE: In case the message did not appear, immediately inform senior.

4.13.1.6 Click OK.

4.14 Click NEXT.

4.14.1 OPTICS PARAMETERS

4.14.1.1 Click <Line Search".

Wait until.

Line Search: OK

Beam Balance: OK

NOTE: If any of these messages did not appear, immediately inform senior.

4.15 Click CLOSE.

4.16 Click FINISH.

4.17 **START MEASUREMENTS.**

4.17.1 Rotate lamp to get maximum lamp and Press Auto Zero.

4.17.2 Leave the lamp ON for at least five minutes.

NOTE: Make sure the sipping tube for aspiration is dipped in double distilled water.

4.17.3 Ignite the flame by simultaneous pressing two ignite buttons (black and white).

4.17.4 Run Standard Solutions (starting with the lowest concentration and auto zeroing in between different concentrations) instrument will plot calibration curves.

4.18 TEST SOLUTION ANALYSIS:

4.18.1 * Run Blank of specific set of samples.

4.18.2 Type the sample ID in the column.

4.18.3 Ignite the flame.

4.18.4 Run the sample solutions for analysis.

4.18.5 Add all collected data from lab notebook, i.e. weight of sample (w), volume of sample (v) and dilution factor (d) to get actual results in ppm of specific element.

4.19 SWITCH OFF THE INSTRUMENT

4.19.1 After running all the samples EXTINGUISH the flame.

4.19.2 Click ON upper right corner on the name of the element and click to switch off the flame.

4.19.3 Switch off the instrument.

4.19.4 Instrument will cut off from the system.

4.19.5 Close all the windows.

4.19.6 Record the results / print out and "log in" the instrument usage with signature, date and time.

4.20 Printed data must bear at least following information:

4.20.1 *True value*

4.20.2 *Concentration*

4.20.3 *Actual concentration*

4.20.4 *Actual concentration Units*

4.20.5 *Volume Factor*

4.20.6 *Weight Factor*

4.20.7 *Dilution factor*

4.20.8 *%RSD*

4.20.9 *Date*

4.20.10 *Time*

4.21 Record / Log in all the data results, and report on paper format.

5. Precautions / Safety:

5.1 Check drain Fill bottle level.

5.2 Check the drainpipe is dipped in waste.

5.3 Close the main supply of gas after use.

5.4 Shut down PC and cover PC/instrument properly before leaving.

5.5 Wear personal protective clothing, goggles and gloves, if needed.

5.6 Only authorized personnel are allowed to operate the system.

6. Related documents / References:

6.1 Operational Instruction Manual Shimadzu Atomic Absorption Spectrophotometer AA-6650.

STANDARD METHOD FOR ANALYSIS OF HEAVY METALS AND MINERALS USING FLAME ATOMIC ABSORPTION SPECTROPHOTOMETER

Standard Method for Analysis of Heavy Metals & Minerals using Flame Atomic Absorption Spectrophotometer

1. Purpose:

This standard testing method is to explain step by step procedure to analyze the metals (Cr, Mg, Ni, Cd, Ca, Pb, Sb, Zn, Fe, Cu, Na, K, Mn, As, Hg) in the samples of raw materials and finished products of different nature and matrix, using Flame Atomic Absorption Spectrophotometer.

2. Scope:

This procedure describes all steps involved in the analysis of heavy metals & minerals in the samples of raw materials and finished products of different matrix using Atomic Absorption Spectrophotometer. This standard testing method is applicable to water, waste water, foods, herbal and pharmaceutical products for determination of followings.

Sr.No.	Element	Detection Limit
1	Cr	0.1ppm
2	Mg	0.1ppm
3	Ni	0.5ppm
4	Cd	0.1ppm
5	Ca	0.5ppm
6	Pb	0.5ppm
7	Sb	5ppb
8	Zn	0.1ppm
9	Fe	0.5ppm
10	Cu	0.1ppm
11	Na	0.5ppm
12	K	0.1ppm
13	Mn	0.1ppm

14	As	5ppb
15	Hg	5ppb

3. **Equipment/Apparatus:**

   3.1. Flame Atomic Absorption Spectrophotometer *(With all related standard solutions and accessories)*

   3.2. Volumetric flasks (10mL, 50mL, 100ml, & 1000 mL).

   3.3. Volumetric pipettes (5 & 10 mL).

   3.4. Pipette Sucker.

   3.5. Funnel.

   3.6. Micropipette (up to 1 mL Capacity).

4. **Reagents/Chemicals required:**

   4.1 Conc.HNO_3 (Analytical/ Reagent grade.).

   4.2 Standard Stock Solution (NIST traceable).

   4.3 Double distilled water.

   4.4 **5% Lanthanum Solution:**

   To prepare 5% (w/v) solution of Lanthanum weigh accurately 58.65 g of La_2O_3 in a 1 Litre beaker, wet the powder with DD water, add slowly and in small amounts 250ml conc.HCl , quantitatively transfer and make to 1 Lit in volumetric flask with DD water.

   4.5 **2% Cesium Solution:**

   To prepare 2 % (w/v) Cesium solution weigh accurately 25.335g CsCl in a 1 Lit volumetric flask, add 86ml conc. HCl and make up the volume using double distilled water.

5. Procedure:

5.1. Environmental Conditions:

Temperature: $(25 \pm 5\ ^{0}C)$

5.2. Preparation of Sample Solution:

5.2.1. Drinking water samples are not required to prepare by ashing while other samples (Herbal and food Products) should be prepared as described in standard method for sample preparation for elemental analysis (Doc. # *TEC-IPL-SMS-01*).

5.3. Preparation of Zero Calibration Solutions:

5.3.1 Prepare zero calibration solution by dissolving 8 mL pure conc. HNO_3 in about 250 mL double distilled water in a 1000 mL volumetric flask and then diluting it up to the mark by adding double distilled water.

5.4. Preparation of Working Solutions:

5.4.1 For 40ppm working standard solution pipette 1mL of standard 1000ppm stock solution with the help of volumetric pipette into clean 25mL volumetric flask and for 200ppm working standard solution pipette 5mL of standard 1000ppm stock solution with the help of volumetric pipette into clean 25mL volumetric flask.

5.4.2 For 1000ppb working standard solution pipette 25µL of standard 1000ppm stock solution with the help of Micropipette pipette into clean 25mL volumetric flask.

5.4.3 Make the volume up to the mark by adding zero calibration solution to prepare working standard/ stock solution.

5.4.4 For determination of Na & K also add 1 ml 2% Cesium solution/ 10ml, while for determination of Ca & Mg add 1ml 5 % Lanthanum solution/10ml of standard samples while making up to the final volume.

Note: All the glassware should be properly washed with detergent and tap water followed by rinsing thrice with distilled water, twice with double distilled water and once with zero calibration soln.

5.5. Standard Curve:

5.5.1. Switch on the Atomic Absorption Spectrophotometer and operate all other steps following work instructions (*TEC-IPL-WI-16*).

5.5.2. Aspirate the zero calibration solution and auto zero the instrument.

5.5.3. Aspirate different standard solutions in ascending order for preparation of standard calibration curve applying standard conditions for the mineral to be analyzed.

Diluted Standard Solutions (For Standard Curve):

Working Standard Solution	**Diluted Standard Solutions**
40ppm	0.1ppm, 0.2ppm, 0.4ppm, 0.8ppm
200ppm	0.5ppm, 1ppm, 2ppm, 4ppm
1000ppb	5ppb,10ppb, 20ppb, 40ppb

5.6. Sample analysis:

5.6.1 Aspirate the zero Calibration solution (Ref 5.3) or sample blank as blank.

5.6.2 Aspirate the sample solution to be analyzed into the flame and in case of default of software note data in lab note book.

6 Quality Checks/ Verification:

6.1. Calibration Curve:

Normally three types of Working Solutions (200ppm, 40ppm, and 1000ppb) are made from stock. Diluted Standard solutions of 0.5ppm, 1ppm, 2ppm and 4ppm are made from 200ppm solution while diluted Standard solutions of 0.1ppm, 0.2ppm, 0.4ppm and 0.8ppm are made

from 40ppm solution. A new calibration curve with freshly prepared standard solutions to be drawn for new estimation.

6.2. Internal quality control (IQC):

For uniformity and stability of the value among samples and triplicates IQC must be run in-between samples and triplicates as well as before and after sample analysis.

6.3. Checking Reproducibility / Verification:

Take reading of the standard solutions periodically in between the samples to ensure proper functioning and reproducibility of instrument response.

NOTE: Especially in case of elements having very low absorption e.g. Ni , Pb etc take extra reading of IQC or Standards after each sample to verify the instrument performance.

6.4. Repeatability of Analysis:

Repeatability of analysis may be determined through replicate sample; at least three replicate must be prepared for each analysis. *

6.5. Analysis Of Old Samples:

Analyze the old samples (previously analyzed at the same conditions using the same procedure in order to verify performance qualification of the instrument and to check the test method

6.6. CRM Analysis (optional):

Periodic analysis of CRM after every three months to assure the system.

6.7. Proficiency Testing:

Participation in PT/ ILC for elemental analysis to verify lab results.

7. Precautions/Safety requirements:

8.1. All the acids should be of analytical grade.

8.2. Use acids and strong / toxic reagents and chemicals with care, under fume hood and with exhaust "TURN ON".

8.3. In case of emergency follow directions given in instruction manual *

8. **References/Related documents:**

9.1. AOAC (1990) Official Methods of Analysis of the Association of Official Analytical Chemists. 15th Ed. pp: 42, 84, 237,312,498,708.

9.2 .Atomic Absorption Spectrophotometery Cookbook Section I. 2000. Basic Conditions for Analysis of Principle of Atomic Absorption Spectroscopy. Shimadzu Corporation, Japan. (Document of external origin HTL-04).

9.3. Work Instructions for Atomic Absorption (AA 6650) Shimadzu. Standard Method for sample preparation for elemental analysis